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Review

Bloom-forming cyanobacteria and cyanotoxins in Argentina: A growing health and environmental concern

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ABSTRACT

Toxic cyanobacterial blooms are a water quality issue worldwide whose incidence and severity are predicted to increase due to climate change and eutrophication. Argentina is not an exception to this trend, since those massive proliferations have increased in the last two decades as a consequence of water quality changes due to human activities. This work presents a thorough search and analysis of published literature on the occurrence of cyanobacterial blooms and cyanotoxins in Argentina. We retrieved 241 bloom events (1944–2014) covering 63 impacted water bodies, used either for recreational activities and/or drinking water supply. The highest incidence was concentrated in the central and eastern areas of the country (Chaco-Pampean Plain and Peripampean Sierras), the most densely populated regions, also highly impacted by agro-industrial activities. Intense blooms of *Microcystis, Dolichospermum* and *Cylindrospermopsis* species represent a potential hazard for both human beings and wild–life through oral ingestion and/or direct contact, although quantitative and systematic registers to estimate the extent of occurrence are still missing. Elevated microcystins concentrations, together with the presence of blooms of potential saxitoxin or anatoxin-a producers emphasize the need to increase monitoring of these toxins in drinking water supplies and recreational areas. The data presented are valuable for promoting the generation and implementation of guideline values and risk management frameworks at a national and regional scale.

1. Introduction

Toxic cyanobacterial blooms represent one of the most conspicuous hazards to human health in freshwater systems (Chorus and Bartram, 1999). They are widely recognized as a water quality issue that affects recreational and drinking water due to the production of potent cyanotoxins [such as microcystins (MCs), saxitoxins, anatoxin-a, and cylindrospermopsins]. At elevated concentrations these cyanotoxins pose a risk to the health of humans, wildlife and wildstock, particularly when ingested (Codd et al., 2005; He et al., 2016).

Anthropogenic eutrophication and climate change seem to play a key role in promoting the proliferation and expansion of toxic cyanobacterial blooms (Heisler et al., 2008; O'Neil et al., 2012; Paerl and Huisman, 2008). The incidence of this phenomenon is predicted to increase in frequency and severity globally, affecting areas previously unaffected (Cheung et al., 2013; Reichwaldt and Ghadouani, 2012). South America is not the exception, although there is scant literature on this subject (Dorr et al., 2010).

In the Southern Cone, Brazil and Uruguay follow the guidance and regulations proposed by the World Health Organization (WHO) regarding the monitoring and management of cyanobacteria and cyanotoxins in drinking and recreational waters, based on parameters that reflect cyanobacterial biomass or MCs concentration (Chorus and Bartram, 1999; WHO, 2003). In particular, these countries have adopted the Guideline Value for MC-LR in drinking water (1 $\mu g\ L^{-1}$ for MC-LR), while guidelines for recreational waters await final approval by the Uruguayan legislation (Vidal and Britos, 2012; Ibelings et al., 2014) and is still under development in Brazil (Azevedo Lopes et al., 2016).

Argentina is a vast country (about 2,800,000 km^2, along 3700 km between 22° and 55° South latitude) located within a region of subtropical and mid-latitude climates. It is endowed with a dense

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hydrographic network which includes rivers, streams, stratified lakes and shallow lakes (Quirós and Drago, 1999). Importantly, 85% of the country's surface water is part of the Rio de la Plata basin (3,100,000 km^2) (Pochat et al., 2006) shared with Brazil, Uruguay, and Paraguay. Even though cyanobacterial blooms have been registered in Argentina since 1944 (Mullor, 1945), reports on massive proliferations have alarmingly increased by the end of 1990's, associated with water quality changes due to human activities (i.e., urbanization, agriculture, untreated effluent discharges) (Pizzolon et al., 1999; Quirós and Drago, 1999). This negatively affects drinking and recreational water quality, resulting in animal mortality and concern of public health impairment (Echenique et al., 2014; Giannuzzi et al., 2011; Mancini et al., 2010; Odriozola et al., 1984; Pizzolon et al., 1999; Quirós and Drago, 1999). In contrast to Uruguay and Brazil, national regulations on risk assessment and management of cyanobacterial or cyanotoxin presence have not been adopted as of yet, albeit the increased concern from the public health community (Otaño et al., 2012). Despite the growing interest in this matter and the research activity conducted on harmful cyanobacterial blooms in the last decades, the scope of the issue has not been fully recognized since reports are scattered and no updated review is available.

The aim of this review is to provide data to better understand cyanotoxin occurrence and thus provide a basis for policy decisions on implementing guidelines or alert level frameworks at the national and regional level.

2. Material and methods

A database was constructed with scientific publications retrieved from Scopus, Google Scholar, and SciELO (to cover some reports and papers in Argentinean publications) from 1945 to 2016, using different word combinations as keywords for titles and abstracts (Argentina; Cyanophyceae; cyanobacteria; blooms; scum; cyanobacterial dominance; and cyanotoxins; as English words; and cianobacteria; floración; cianotoxinas; as Spanish words). Studies on freshwater systems that mention the word "bloom" or included quantitative data (such as chlorophyll *a*; cyanobacterial biovolume or cyanobacterial cell counts) albeit not mentioning the term "bloom" *per se* were considered. Cyanobacterial bloom reports that provided no data on dominant species were excluded from the data set. When different papers referred to the same water body and study period; the most informative one was analysed. Information was taken from international and national journals (n = 50); book chapters (n = 3); proceedings (n = 8); conference presentations (n = 9); and technical reports (n = 7). When needed; we clarified or corroborated data by contacting the authors directly (personal communications).

Each quantitative datum was classified in categories following the Alert Levels Framework and the Guidance Levels for drinking and bathing waters, respectively, proposed by WHO (Chorus and Bartram, 1999; WHO, 2003). Quantitative values corresponding to Alert Level 1 (2000 cells mL^{-1}, or 0.2 mm^3 L^{-1} biovolume, or 1 μg L^{-1} chlorophyll *a* in the water body) were considered as a cyanobacterial bloom. Taxa were recorded at species level; however, if species information was not available in a report, we recorded data at the genus level to avoid missing information. Taxonomy was updated according to recent literature whenever possible.

Kruskal-Wallis H tests were used to explore differences between affected ecosystems (lentic, lotic and reservoirs), and Dunn's multiple comparison tests were conducted as *post hoc*, with $p < 0.05$ considered significant. Analyses were performed with SigmaPlot version 11 (Systat Software, Inc).

Maps were elaborated using GIS software ArcMap 10.1. Vector data on administrative limits, water bodies and land cover were downloaded from Instituto Geográfico Nacional (IGN) as shape files (http://ign.gob.ar/sig). Six major geographic lake regions were recognized and digitalized according to Quirós and Drago (1999).

3. Results and discussion

3.1. Main characteristics and geographic distribution of blooms

The literature yielded 241 bloom events and 110 georeferenced data covering 63 water bodies [rivers, estuaries and streams (n = 11), stratified lakes, shallow lakes and ponds (n = 33), reservoirs and dams (n = 19)] affected by blooms at least once. Reports of bloom occurrence before 1999 and between 1990 and 2000 were scarce (3% and 10% of the 241 events, respectively), as compared to reports after 2000 (87%). Even though reports on massive proliferations have risen notoriously since the beginning of this century, since more research groups are getting involved in this topic and, consequently, more studies are published nowadays such increase may not necessarily imply a higher frequency in bloom occurrence. Therefore, we do not discard a possible bias in reported data.

Sampling frequency was not homogeneous (it differed between water bodies and varied from a single sampling to hourly, weekly, fortnightly and monthly sampling, see for example Grosman and Sanzano, 2002; Izaguirre et al., 2015; Sathicq et al., 2014). Such heterogeneity prevented any analysis of the relationship between the number of samples per water body and the frequency of blooms registered. Some publications that contained the word "bloom" (n = 20) included neither quantitative values nor comments on the appearance of phenomena such as scums in the littoral zone and/or changes in water colour. This highlights the lack of a clear definition and the ambiguity in the use of the term "bloom" in the literature. Soares et al. (2013) also report the lack of information in terms of the visual appearance of blooms in Brazil. The inclusion of observational and describing data in cyanobacterial studies would be useful to better appreciate the extent of these phenomena.

The reported cyanobacterial blooms are located along and across the country from North (25° 18′ 0″ N) to South (54° 35′ S) and from East (55° 0′ W) to West (71°16′ W), in a wide range of climatic lentic environments and areas used for intensive agriculture (Figs. 1, S1). The main geographic lake region affected is the Chaco-Pampean Plain (n = 212, 88% of all 241 reports, region 2), followed by the Peripampean Sierras (8%, region 3) and the Patagonian Plateau (4%, region 5). Reports from the Andean Patagonia (region 4) and Misiones Plateau (region 6) are scarce (n = 3 and n = 1, respectively), and no information was retrieved from the Puna (region 1). In general, cyanobacterial dominance was most pronounced during the warmest months, as reported from other temperate climates (Chorus and Bartram, 1999; Jöhnk et al., 2008). Blooms started earlier and persisted longer in the subtropical North. In subtropical and temperate regions (Chaco-Pampean Plain and Peripampean Sierras), peaks of cyanobacterial biomass developed in summer (n = 97, 44%) and mid-summer until mid-autumn (n = 92, 42%). Some blooms extended from spring to summer (n = 6, 2.7%) while reports on cooler seasons and along the whole year (perennial) were scant (less than 2%). Cyanobacterial dominance was restricted to summer in cold-temperate climate lakes (Patagonian Plateau and Andean Patagonia).

The Chaco-Pampean Plain region extends from the centre to the northern and eastern areas of Argentina, and it is characterized by an edaphic heterogeneity and a large climatic variety (from North to South: subtropical and temperate climates) (Fig. 1B, S1) (Quirós and Drago, 1999). This region concentrates more than 50% of the country's population (about 29 million inhabitants) which mainly live in urban areas (INDEC, 2010). The Río de la Plata Basin, the fifth largest basin in the world and the second largest in South America, comprises the Paraná, Paraguay and Uruguay rivers, and the Río de la Plata River (Tundisi et al., 1998), and sustains the region for drinking water supply, generation of hydro-electric power and agriculture. Most cereal and oilseeds are grown in this region, and it is used for breeding most of the country livestock (WWAP, 2007). Additionally some of the largest reservoirs in South America are on the tributaries of Río de la Plata basin.

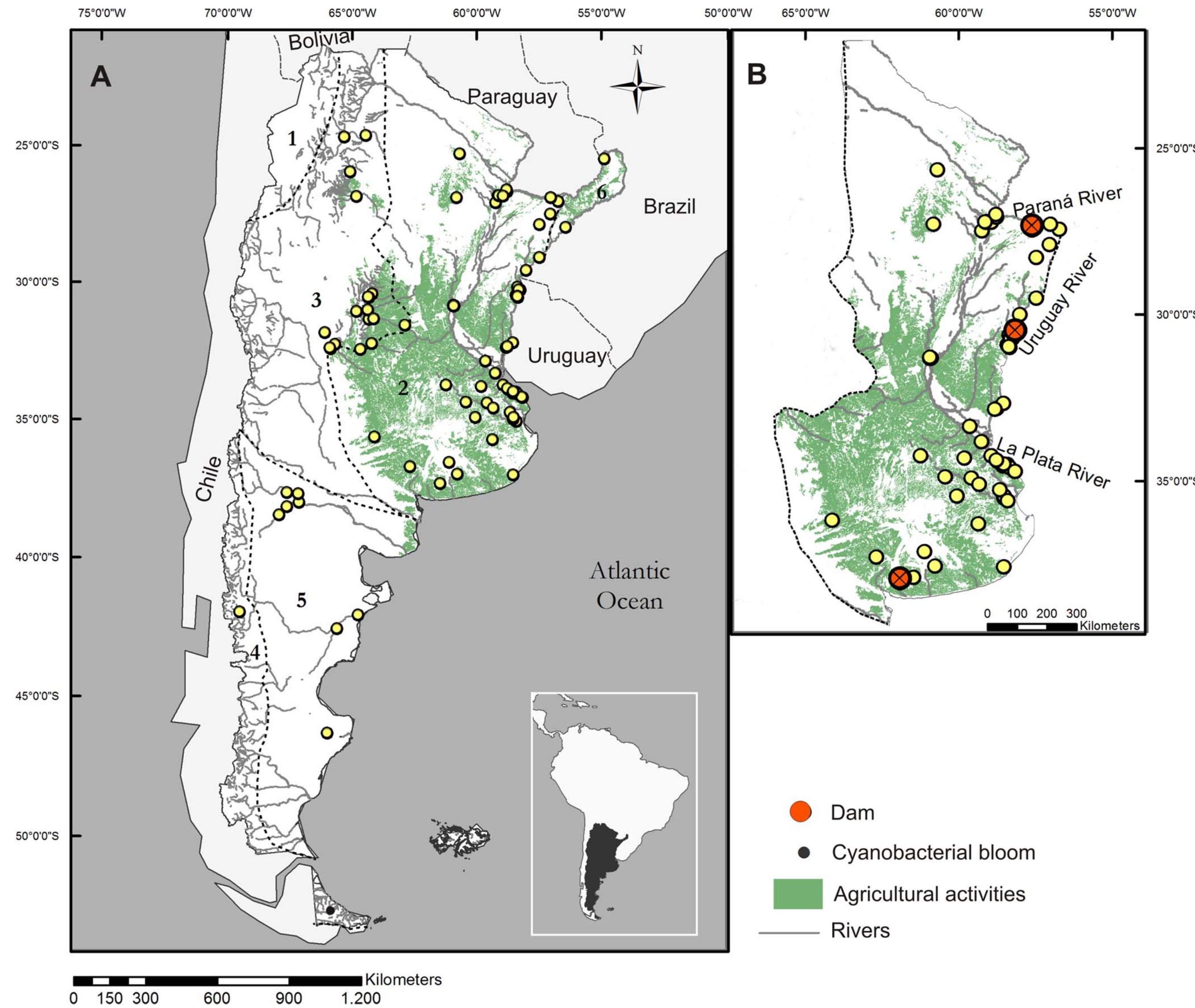

Fig. 1. Distribution of cyanobacterial bloom reports evaluated from Argentina (1945–2014). (A) Map of Argentina showing bloom locations. (B) Chaco-Pampean Plain region. Numbers indicate geographical lake regions, according to Quirós and Drago (1999): 1, Puna; 2, Chaco-Pampean Plain; 3, Peripampean Sierras; 4, Andean Patagonia; 5, Patagonian Plateau; 6, Misiones Plateau.

In particular, Yacyretá (27° 28′ S, 56° 44′ W) and Salto Grande dams (30°53′ S, 57°58′ W) (on the Paraná River and Uruguay River, respectively), which are not only important drinking water and electric power suppliers, but also serve as leisure areas (Chalar et al., 2002; Meichtry de Zaburlín et al., 2013). Finally, the central part of the Chaco-Pampean Plain (known as the Pampean region) has thousands (> 150,000) of shallow lakes and microbasins (from 0.01 ha to water bodies larger than 10 ha) (Dangavs, 2005; Diovisalvi et al., 2015; Geraldi et al., 2011).

The quality of the water resources located in the Chaco-Pampean Plain has been significantly deteriorated by a combination of human activities, chiefly urbanization, deforestation, hydropower developments, agriculture, industrial activities, and tourism (Quirós and Drago, 1999; Tundisi et al., 1998; WWAP, 2007). Key freshwater bodies of the Chaco-Pampean Plain region used for drinking water, fisheries and recreation are highly vulnerable to pronounced mass cyanobacterial development due to the progressive eutrophication caused by human activities (FREPLATA, 2006; Izaguirre et al., 2012, 2015). Additionally, the construction of a large number of reservoirs on the rivers of the Río de la Plata basin has led to the transformation of lotic into lentic or semi-lentic ecosystems, which are much more prone to cyanobacterial blooms (Meichtry de Zaburlín et al., 2013; O'Farrell et al.,2012). Limnological studies performed downstream of the dams revealed their significant impact on aquatic communities and their contribution to cyanobacterial proliferation. Toxic cyanobacterial blooms have been recently reported in the Uruguay River, downstream Salto Grande dam (O'Farrell and Izaguirre, 2014), and in the Paraná River, downstream the Yacyretá dam (Forastier et al., 2016).

The Peri-Pampean Sierras region (región 3, Fig. 1A) comprises the arid western corridor, characterized by high and low mountain ranges and semi-arid valleys (Quirós and Drago, 1999). The region is home to several reservoirs used mainly to irrigate crops, generate hydroelectric power and supply drinking water (Casco and Mac Donagh, 2014). Many are notoriuosly affected by human activities thereby increasing eutrophication and, consequently, cyanobacterial proliferation (Casco and Mac Donagh, 2014; Quirós and Drago, 1999; Ruiz et al., 2013). Reservoirs used to supply drinking water are often monitored by local or provincial authorities and results are not reported into published literature or official national databases. Consequently, significant amount of information may remain inaccessible. Few investigations have been conducted on the remaining water bodies (Casco and Mac Donagh, 2014). Therefore, the occurrence of cyanobacterial blooms may be

considerably underestimated in this region.

Toxic cyanobacterial blooms have been registered in the most important dams in the region: San Roque (31°21′ S, 64°30′ W), Los Molinos (31°50′ S, 64°25′ W), Cruz de Piedra (33°00′S 66°12′ W), Cabra Corral (25° 18′ 0″ S, 65° 25′ 0″ W), and El Tunal (25° 15′ 8″ S, 64° 31′ 40″ W) (Amé et al., 2010; Casco and Mac Donagh, 2014; Cossavella et al., 2011; Ruiz et al., 2013; Salusso and Moraña, 2014; Silva et al., 1995).

Cyanobacterial blooms were also reported in the northern and central eastern Patagonian Plateau, a cool and dry region, with long winters, characterized by a basaltic plateau and tectonically uplifted pebble fans (region 5, Fig. 1, Fig. S1) (Quirós and Drago, 1999). Poor water quality has been reported in reservoirs located in rivers used for water supply, irrigation and fish farming (Quirós and Drago, 1999). In the North, the Limay River (38°59′35″ S, 68°00′18″ W), the Ramos Mexía dam (39°17′00″S, 68°48′00″ O) and the Mari Menuco dam (38°35′49″ S, 68°32′41″ W, on the Neuquén River) are the main water bodies affected by blooms of toxic species (Alcalde et al., 1996; Casco et al., 2014; Echenique et al., 2014; Guarrera et al., 1995; Othaz Brida et al., 2010). In the eastern Patagonian Plateau, blooms have been reported in the Florentino Ameghino dam (43°42′S; 67°27′W), used for the provision of hydroelectric power, flood retention, irrigation and potable water (Pizzolon et al., 1999; Casco et al., 2014).

Future climate change scenarios predict changes in patterns, intensities and duration of precipitation and droughts, with consequences for cyanobacterial dominance and development in eutrophic waters (Paerl and Paul, 2012). Elevated rainfall and flushing events followed by periods of drought with increased residence times and internal cycling of nutrients promote mass development of cyanobacteria, a pattern already seen in multiple systems worldwide including Australia, South Africa and USA (Paerl and Huisman, 2009). According to recent studies, an increase in drought severity is expected in central-west Argentina and in northern Patagonia (region 3 and 5) (Penalba and Rivera, 2013). Alterations in weather patterns, together with hydrologic modifications in this region (reservoir constructions) and antropogenic eutrophication could yield larger and more sustained harmful cyanobacterial bloom events in these regions.

3.2. Toxigenic taxa

Toxigenic Nostocales, Chroococcales, Synechococcales and Oscillatoriales species were found in Argentinean freshwater bodies. Members of the three first taxonomical orders yielded the widest distribution (Fig. 2). Bloom composition differed in lotic and lentic freshwater systems and also between geographic and climatic regions. While Chroococcales predominated in rivers, the co-dominance of members of different orders was frequently detected in dams and shallow lakes (Fig. 3A). *Microcystis* sp. (Chroococcales) were the most prevalent bloom-causing cyanobacteria in Argentinean water bodies (n = 203, 49%), and particularly found as the dominant genus in subtropical and temperate rivers and streams (n = 110, 67%) (regions 2 and 3; Fig. 3B). *Microcystis* species were absent in cold-temperate regions (4 and 5). *Dolichospermum* (n = 132, 32%), *Raphidiopsis* (5%) and *Cylindrospermopsis* (3%) were the most common Nostocales genera, followed by the Oscillatoriales *Planktothrix* and *Pseudanabaena* (< 1%). *Dolichospermum* species yielded the widest distribution. While blooms of *D. circinale, D. spiroides* and *D. lemmermannii* were recorded in cold-temperate regions, *Dolichospermum* species were commonly found together with *Microcystis* (mainly *M. aeruginosa* and *M. wesenbergii*) in subtropical reservoirs and rivers. Lentic water bodies presented greater variability regarding bloom composition. Blooms of Synechococcales of the genera *Snowella*, *Planktolynbya*, and *Coelosphaerium* were only reported in this type of freshwater systems (Fig. 3). Table 1 summarizes the species found most frequently in Argentina.

The most prevalent genera found in Argentinean freshwater bodies (*Microcystis, Dolichospermum, Cylindrospermopsis*) are also reported as the most frequent ones in blooms in Brazil, Uruguay, and outside the continent (O'Neil et al., 2012; Soares et al., 2013; Bonilla, personal communication). The co-occurrence of *Dolichospermum* and *Microcystis* species, frequently observed in Argentina (Echenique et al., 2006; Fernández et al., 2009; O'Farrell et al., 2012; Ruiz et al., 2013) has also been reported in tropical Brazilian and Colombian reservoirs (Palacio et al., 2015; Sotero-Santos et al., 2008). According to Mowe et al. (2015), most blooms in tropical America are formed by *Microcystis* and *Cylindrospermopsis* species. MC-producers strains of *Microcystis* (mainly *M. aeruginosa*) are widespread in freshwater ecosystems worldwide (Harke et al., 2016; Humbert et al., 2013). *Cylindrospermopsis raciborskii*, known cylindrospermopsin and saxitoxin producer, is expanding its distribution from the tropics to temperate regions (Bonilla et al., 2016; Burford et al., 2016; Padisák, 1997; Sukenik et al., 2012). Blooms of this species occurred in the Uruguay River (subtropical climate) in co-dominance with *P. agardhii* and *Raphidiopsis* species (Otaño, 2009a). Notably, *C. raciborskii* has been recently reported in the Pampean region, the most southern register in the temperate South America (34°54′25″S) (Cremaschi et al., 2015). *Raphidiopsis mediterranea*, a subtropical species known to produce cylindrospermopsins and anatoxin-a (Namikoshi et al., 2003; Rzymski and Poniedziałek, 2014) was frequently found in water bodies in northern Argentina (Forastier and de Domitrovic, 2014; o, 2009a, 2009b; Otaño, 2009b), and in shallow lakes in the Pampean region (region 2, Fig. 1) (Aguilera et al., 2013; Allende et al., 2009; Izaguirre et al., 2012, 2015; O'Farrell et al., 2014). *Planktothrix agardhii* was reported in temperate eutrophic shallow lakes forming perennial blooms, often associated with fish mortality (Aguilera et al., 2013; Alvarez et al., 2009; Bauzá et al., 2014; Martínez de Fabricius et al., 2014). Such perennial blooms of *P. agardhii* have been often documented in European temperate, hypertrophic shallow lakes (Yéprémian et al., 2007).

3.3. Cyanotoxins and volatile compunds

Information on cyanotoxins occurrence in Argentinean freshwater bodies is still scant. There are sporadic or single reports (Forastier et al., 2016; Mancini et al., 2010; Otaño, 2009a) and few available historical data restricted to some specific rivers and reservoirs (Ruibal Conti et al., 2005; Giannuzzi et al., 2012; Ruiz et al., 2013; Sathicq et al., 2014).

From our data set, 118 of the 241 reported cyanobacterial blooms (62%) that we evaluated were positive for toxins. Cyanotoxins were recorded in several regions, particularly in central and north-eastern areas of Argentina (Table 2, Fig. 4A). MCs were the toxins most frequently found (n = 112), and reservoirs accounted for the highest concentrations (Dunn's multiple comparison test; $p < 0.05$). Reports on the presence of saxitoxins and anatoxin-a were scant (n = 2 and n = 1, respectively) (Table 2, Fig. 4B). Rather to be associated with null (cylindrospermopsins) or scarce (saxitoxins and anatoxins) cyanotoxin occurrence, such low report frequency is likely to be related to the low number of laboratories that actually measure cyanotoxins other than MCs in Argentina.

The fact that MCs are the most widespread and frequently detected cyanotoxins in Argentina, is in line with other reports from South America (Bittencourt-Oliveira et al., 2014; Bonilla et al., 2015; Dorr et al., 2010) and the rest of the world (WHO, 2003; Ibelings and Havens, 2008; Ibelings et al., 2014). However, the growing concern associated with cyanobacteria and their toxic blooms has caused that more laboratories become involved in cyanotoxin research worldwide (Merel et al., 2013). As a consequence, reports on the occurrence of other cyanotoxins such as saxitoxins, anatoxin-a(s) and cylindrospermopsins become available in South America (Bittencourt-Oliveira et al., 2011; Bittencourt-Oliveira et al., 2014; Bonilla et al., 2015; Mowe et al., 2015), highlighting the need of assessing and managing the health risks they pose. Even though cylindrospermopsins have not been reported so far in Argentinean, the presence of known cylindrospermopsins producers, such as species of *Cylindrospermopsis*,

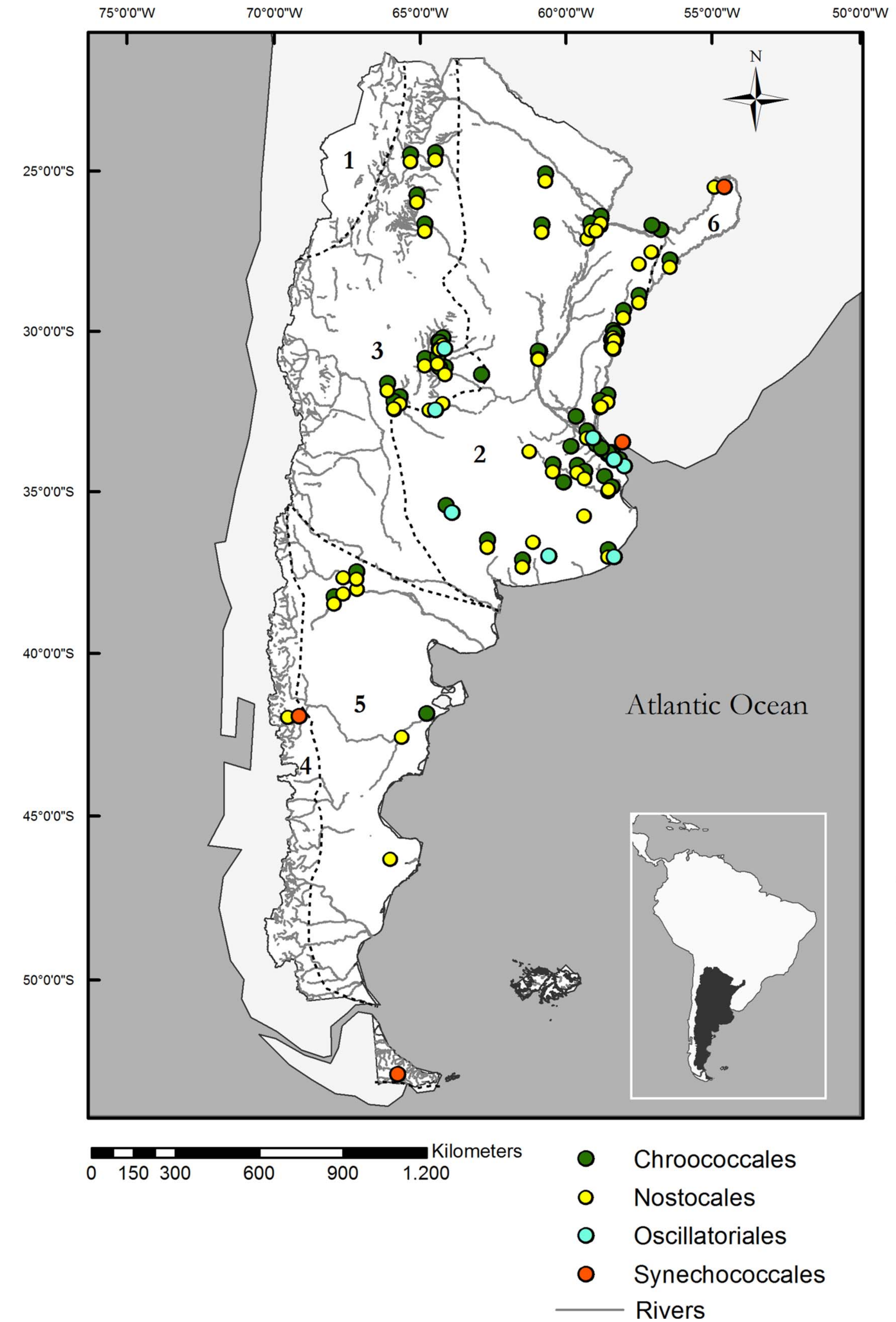

Fig. 2. Distribution of cyanobacterial taxonomical orders reviewed from Argentinean freshwater bodies. Numbers indicate geographical lake regions as indicated in Fig. 1.

Raphidiopsis and *Aphanizomenon* (Burford et al., 2016; Cirés and Ballot, 2016; McGregor et al., 2011), emphasize the need to monitor that toxin in our water bodies.

The limited literature on toxin concentration or production (26% of the 241 bloom events) could be attributed to the fact that most studies are focused on phytoplankton dynamics rather than cyanotoxin

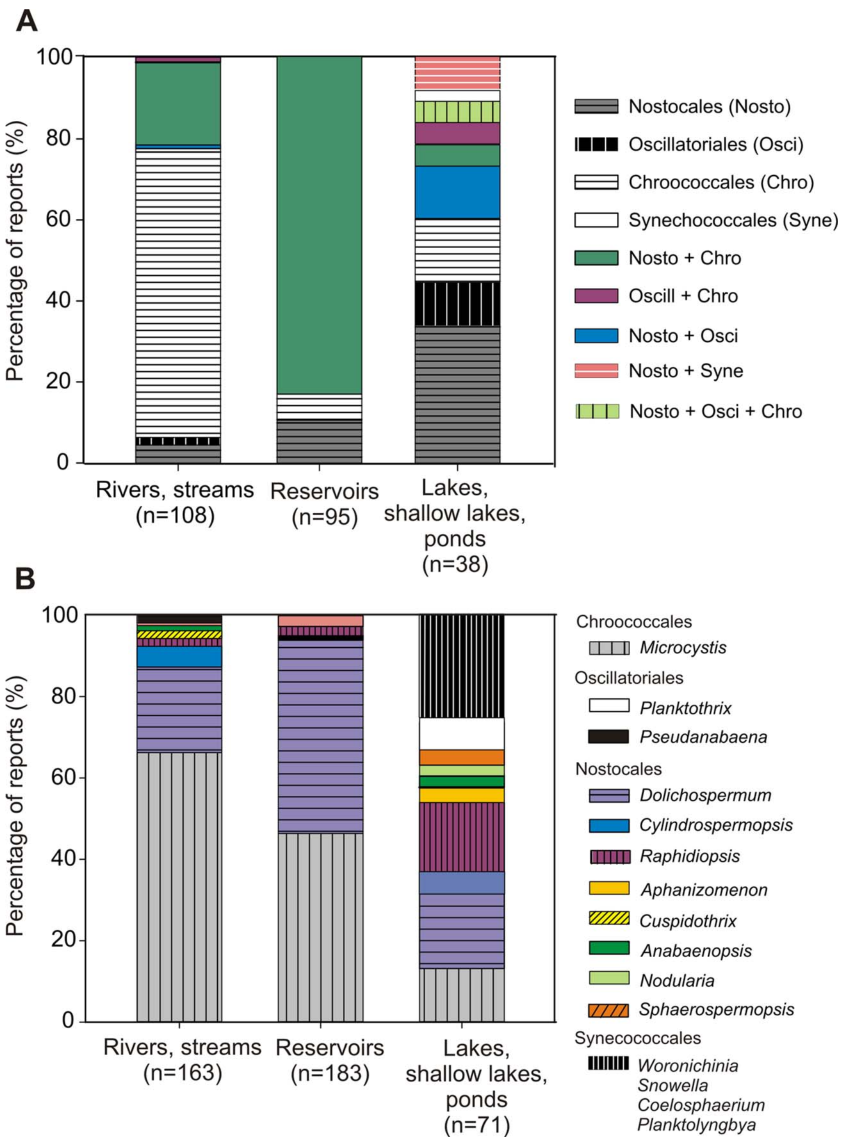

Fig. 3. Cyanobacterial taxonomical orders and genera reported in 241 Argentinean blooms (1945–2014). (A) Proportion of dominance and co-dominance of cyanobacterial orders. (B) Predominant genera.

occurrence (e.g. Allende et al., 2009; Izaguirre and Vinocur, 1994; Izaguirre et al., 2015; O'Farrell et al., 2014). Moreover, many cases of harm to livestock or animal mortality (fish, birds) associated with cyanobacterial blooms have not been tested for toxins (Colautti et al., 1998; Grosman and Sanzano, 2002; Ehrenhaus and Vigna, 2006; Mancini et al., 2010; Odriozola et al., 1984). The lack of data regarding cyanotoxin detection and quantification, even for MCs, could be explained by the costs of testing methods entailed in cyanotoxin analytical standards, equipment and trained personnel. Routine monitoring is not usually carried out by the few laboratories that have HPLC and/or mass spectrometry equipments.

We conclude that in spite of the limited number of toxin registers as

Table 1
Cyanobacterial taxa registered in blooms in Argentinean freshwater bodies.

Order	Taxa	References
Chroococcales	*Microcystis flos-aquae, Microcystis aeruginosa, Microcystis panniformis, Microcystis wesenbergii, Microcystis* spp.*, Radiocystis fernandoy*	Aguilera et al., (2013, 2016); Allende et al. (2009); Amé et al. (2010); Bauzá et al. (2014); Bogarín et al. (2012); Casco and Mac Donagh (2014); Chalar et al. (2002); Colautti et al. (1998); Cremaschi et al. (2015); Echenique et al. (2006, 2014); Ehrenhaus and Vigna (2006); Fernández et al. (2009); Forastier et al. (2016); Forastier and de Domitrovic (2014); Giannuzzi et al. (2012); Grosman and Sanzano (2002); INA-FREPLATA (2012); Izaguirre et al. (2015, 2012); Izaguirre and Vinocur (1994); Mancini et al. (2010); Martínez de Fabricius et al. (2014); Meichtry de Zaburlín et al. (2013); Odriozola et al. (1984); Farrell et al. (2014, 2012); O'Farrell and Izaguirre (2014); o (2009a, 2009b); Pizzolon et al. (1999); Rodriguez et al. (2012); Ruibal Conti et al. (2005); Ruiz et al. (2013); Salusso and Moraña (2014); Sathicq et al. (2014); Werner et al. (2011)
Synechococcales	*Aphanocapsa delicatissima, Cyanodictyon* sp.*, Merismopedia tenuissima, Snowella lacustris, Planktolynbya, Coelosphaerium* sp.	
Oscillatoriales	*Oscillatoria tenuis, Oscillatoria* sp.*, Planktothrix agardhii, Pseudanabaena limnetica, Pseudanabaena mucicola, Pseudoanabaena* sp.	
Nostocales	*Anabaena catenula, Anabaena inaequalis, Anabaena variabilis, Anabaenopsis circularis, Anabaenopsis* cf. *cunningtonii, Anabaenopsis elenkinii, Aphanizomenon flos-aquae, Aphanizomenon* spp.*, Cuspidothrix issatschenkoi, Cylindrospermopsis raciborskii, Dolichospermum circinale, Dolichospermum flos-aquae, Dolichospermum lemmermannii, Dolichospermum planctonicum, Dolichospermum solitarium, Dolichospermum spiroides, Dolichospermum* sp. (ex *Anabaena*)*, Nodularia spumigena, Nodularia* sp.*, Raphidiopsis curvata, Raphidiopsis mediterranea, Sphaerospermopsis aphanizonemoides, Sphaerospermopsis torques-reginae*	

Table 2
Cyanotoxins and volatile compounds registered in water bodies of Argentina.

Type of water body	Limnological region	Name of water body	Uses	Potential toxic species found	Toxin test	Highest amount of toxins (μg L^{-1})	Volatile Compounds (ngL^{-1})	Effect	Reference
Rivers, streams									
	Chaco-Pampa Plain	Río de la Plata Estuary	WS;RA;F	*M. aeruginosa* *M. tenuissima*	HPLC; HPLC-UV; Mouse bioassay	MC-LR: 8.6	nd	MC in domiciliary drinking water	Andrinolo et al. (2007); Echenique et al. (2014), Giannuzzi et al. (2012); Sathicq et al. (2014);
	Chaco-Pampa Plain	Salado River	WS;RA;F	*R. curvata* *R. mediterranea* *C. raciborskii* *P. agardhii*	HPLC	STX: 105.33	nd	nd	Otaño (2009a); Otaño et al. (2012)
	Chaco-Pampa Plain	Uruguay River	WS;RA;F	*M. aeruginosa* *M. wesenbergii* *D. spiroides* *D. circinale* *C. raciborskii,* *Aph. chindleri*	ELISA, LC/MS, GC/MS	MC: 0.6; STX: 0.31; ANTX-a: 0.055	Geosmin:463 2-MIB: 2	nd	Bogarín et al. (2012); Otaño et al. (2012)
	Chaco-Pampa Plain	Paraná river	WS;RA;F	*M. aeruginosa*	HPLC-PDA	MC-LR: 1.9; MC-RR: 1.23 [D-Leu1] MC-LR: 37.7	nd	nd	Forastier et al. (2016)
	Patagonian plateau	Limay River	WS;RA;F	*D. circinale* *D. spiroides* *D. lemmermannii*	Mouse bioassay	(+) possibly neurotoxins	nd	nd	Alcalde et al. (1996); Echenique et al. (2014)
Reservoirs, dams									
	Chaco-Pampa Plain	Paso de las Piedras	WS;RA;F	*D. circinale* *M. aeruginosa*	ELISA, LC/MS, GC/MS	MC: 0.170	Geosmin: 1000	Bad odors; cyanobacterial cells in drinking water;	Ruibal Conti et al. (2005); Echenique et al. (2006, 2014)
	Chaco-Pampa Plain	San Roque	WS;RA;F	*Microcystis* sp. *Anabaena* sp. *Pseudoanabaena*	HPLC-UV; ESI–MS/MS; LC/MS	MCs: 920 (MC-LR, RR, YR) ANTX: 0.0066		MC-LR (2 μg L^{-1}) in recreational waters (beaches); MC content in edible fish (muscle and liver)	Ruibal Conti et al. (2005); Cazenave et al. (2005); Ruiz et al. (2013);
	Chaco-Pampa Plain	Piedras Moras	WS;RA;F	*A. spiroides* *M. aeruginosa*	ELISA	MCs: 0.23		Wild-life death/ decease, (birds).	Mancini et al. (2010)
	Chaco-Pampa Plain	Los Molinos	WS; RA; fi	*Microcystis* sp.		MCs			Casco and Mac Donagh (2014); Cossavella et al. (2011)
	Chaco-Pampa Plain	Salto Grande	WS;RA;F	*M. wesenbergii* *M.aeruginosa* *Dolichospermum* sp.	HPLC-PDA	MC-LR: 48.6		Acute Intoxication in humans	Giannuzzi et al. (2011)
	Patagonian plateau	Ramos Mexía		*D. circinalis,* *D. spiroides* *D. lemmermannii*	Mouse bioassay	(+) possibly neurotoxins		Vigilance and Alert Levels; Weekly reporting to drinking water suppliers	Alcalde et al. (1996); Casco and Mac Donagh (2014); Echenique et al. (2014)

(continued on next page)

Table 2 (*continued*)

Type of water body	Limnological region	Name of water body	Uses	Potential toxic species found	Toxin test	Highest amount of toxins (μg L^{-1})	Volatile Compounds (ngL^{-1})	Effect	Reference
Lakes, shallow lakes, ponds									
	Chaco-Pampa Plain	de los Padres	RA;F	*Microcystis* sp. *P. agardhii Dolichospermum* (ex *Anabaena*)	HPLC–MS/MS	Mean total Mc 7.60 ± 8.08 MC-LR: 0.32; MC-RR: 12.3; MC-LA: 2.14; MC-YR: 0.13		MC content in edible fish (muscle and liver)	Amé et al. (2010)
	Patagonian plateau	Zeta Lagoon	RA;F	*A. spiroides Aphanizomenon* sp	HPLC	MC-RR; MC-YR; MC-LR		nd	Otaño et al. (2012); Pizzolon (2002)

ANTX, anatoxin-a;ELISA, enzyme-linked immunosorbent assay; ESI–MS/MS, electrospray tandem mass spectrometry; F, fishing; GC/MS, gas chromatography–mass spectrometry; HPLC, quantitative high-performance liquid chromatography; LC/MS, liquid chromatography mass spectrometry; MC, microcystin; nd, not determined; PDA, photo-diode array; RA, recreational activities; STX, saxitoxin; UV, standard ultraviolet detector; WS; water supply.

compared to bloom reports the risk of exposure to toxigenic cyanobacteria and cyanotoxins through freshwater could well be high in Argentina, particularly in Chaco-Pampean Plain and Peripampean Sierras (regions 2 and 3) (Fig. 4A).

Within the volatile compounds, geosmin and 2-methylisoborneol were the most frequently reported in Argentinean freshwater bodies (Echenique et al., 2006, 2014) (Table 2, Fig. 4A). Geosmin and 2-methylisoborneol cause offensive tastes and odors in drinking and recreational water (Watson et al., 2016), affecting people's behaviour albeit not being toxic in concentrations found in the environment (Burgos et al., 2014). In extreme cases, volatile compounds can affect treatment plant operation, resulting in substantial costs, and cause severe drinking water shortages. An extreme case was the 'Wuxi crisis' in Lake Taihu (China), where the water supply to over 2 million residents was closed for five days due to organosulfur-derived odors produced by cyanobacteria (Ma et al., 2013). Cases of offensive odour in drinking water have been reported in Cruz de Piedra lake (Silva et al., 1995) and Paso de las Piedras reservoir (Echenique et al., 2006) (Table 2). In Paso de las Piedras, reports of dermic reactions and respiratory problems in the consumer population were associated with the alterations in drinking water quality due to *D. circinale* which also produced geosmin (Echenique et al., 2006).

3.4. Exposure routes to cyanobacteria and cyanotoxins

Argentinean freshwater bodies affected by blooms are used for recreational purposes, or for both drinking water and leisure (Fig. 5A). Reservoirs represent the greatest risk of exposure to cyanobacteria through recreational use (Dunn's multiple comparison test; $p < 0.05$) (Fig. 5B). Most blooms (n = 82, 85%) contain more than 10^5 cyanobacterial cells mL^{-1} (WHO Guidance level 2, Fig. 5B–C) (O'Farrell et al., 2012; Ruiz et al., 2013). A case of acute human intoxication due to oral ingestion of bloom water was registered in a recreational area at the Salto Grande reservoir (Giannuzzi et al., 2011) (Table 2). In rivers, 44% of blooms (n = 64) are within WHO Guidance level 1, whereas 30% exceeded Guidance level 2. In lentic water bodies, the occurrence of blooms with more than 10^5 cyanobacterial cells mL^{-1} reached 50%, which implies a risk of exposure in lakes and shallow lakes used for recreational purposes (Fig. 5B–C).

MC concentrations in water bodies used for drinking-water supply frequently exceed the provisional WHO guideline for drinking water (1 μg L^{-1}) (Chorus and Bartram, 1999; WHO, 2003). MC-LR concentrations between 0.02 μg L^{-1} and 8.6 μg L^{-1} were detected in *M. aeruginosa* blooms in recreational areas of Río de la Plata River and near the main intake of La Plata city water treatment plant (Giannuzzi et al., 2012). Concentrations of [D-Leu1] MC-LR between 6.9 and 37.7 μg L^{-1} were related to *M. aeruginosa* blooms in the Paraná River, the main source of drinking water for the north-eastern region (Forastier et al., 2016). In the San Roque reservoir, the main supplier of drinking water to Córdoba city (1.3 million inhabitants) (Ruiz et al., 2013), total MC concentrations ranged from 0.03 to 798.90 μg L^{-1} in recreational areas, and from 0.07 to 136 μg L^{-1} at water intake areas (Ruibal Conti et al., 2005). In the Salto Grande reservoir, 48.6 μg L^{-1} of MC-LR were registered in blooms of *M. aeruginosa* and *M. wesenbergii.* Data on concentrations in finished drinking water are not available for any of these sites. Total MC concentrations between 0.22 and 14.96 μg.L^{-1} were measured in the recreational waters of Los Padres shallow lake (region 2; 37°56′17″ S, 54°44′11″ W), where blooms of *P. agardhii*, *Anabaena* sp. and *Microcystis* occurred (Amé et al., 2010) (Table 2).

The saxitoxin concentrations reported in the Paraná River (105.33 μg.L^{-1}) associated with blooms of *R. curvata, R. mediterranea*, *C. raciborskii* and *P. agardhii* (Otaño, 2009a), surpassed the guidance values for saxitoxins (3 μg L^{-1}) adopted by countries such as Australia, Brazil and New Zealand (Ibelings et al., 2014). The anatoxin-a concentration reported from the San Roque reservoir (6.6 ng L^{-1}) was 500–1000 times lower than the provisional guideline adopted by

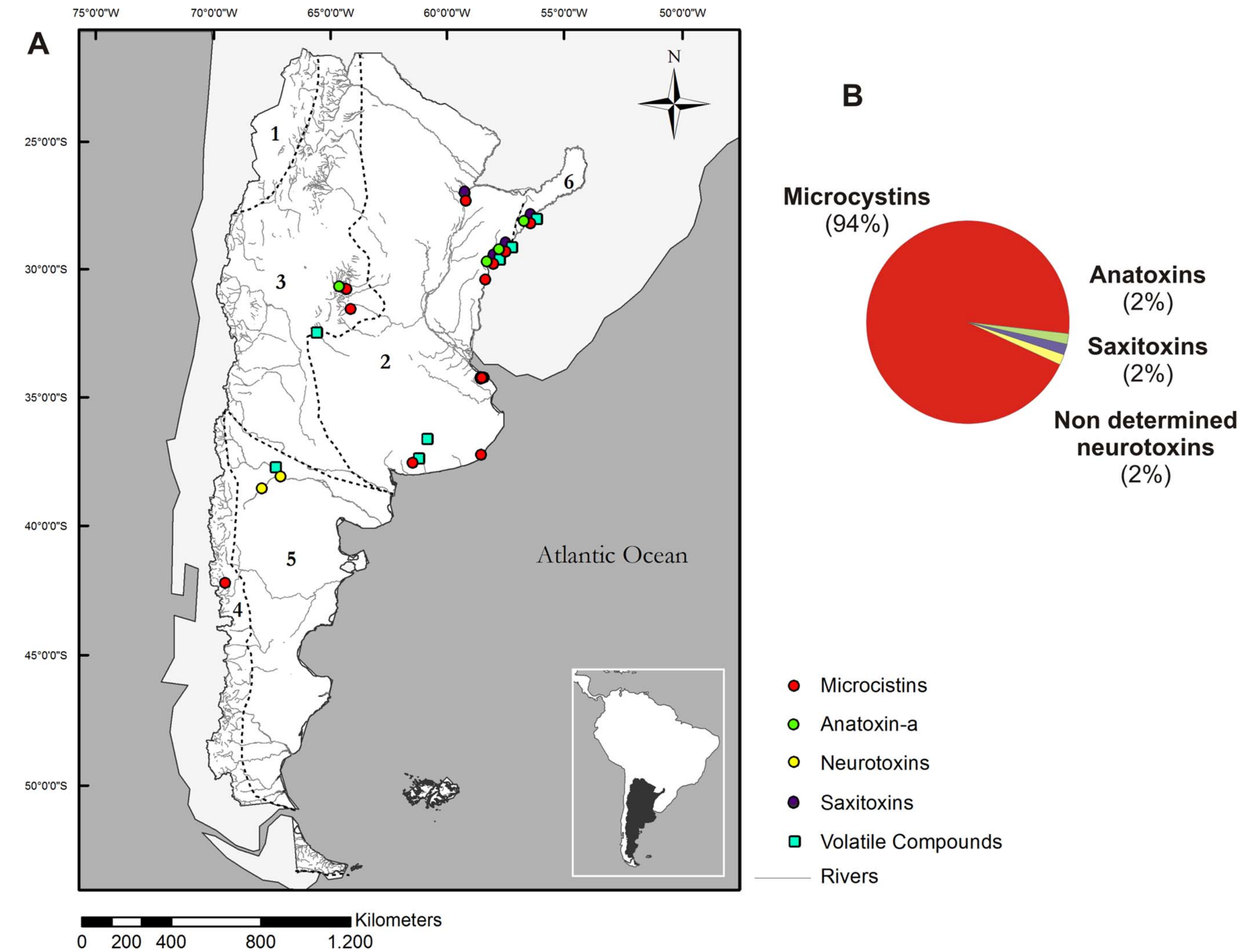

Fig. 4. Cyanotoxins and volatile compounds in Argentinean freshwater bodies reported between 1995 and 2014. (A) Localization of cyanotoxins and volatile compounds. Numbers indicate geographical lake regions as indicated in Fig. 1. (B) Relative contribution of different cyanotoxins (n = 118 reports).

Canada and New Zealand for drinking water, respectively (Ibelings et al., 2014).

Concerning potential cyanotoxin exposure through food, Cazenave et al. (2005) detected MC–RR in fish (gills, liver, muscle) usually captured and consumed by humans in San Roque dam. Also, Amé et al. (2010) found MC–LR, −RR, −LA and −YR in fish tissues (liver and muscle) collected in Los Padres shallow lake (Table 2). Nonetheless, as far as we have investigated, human exposure to contaminated food has not been quantified in Argentina.

4. Risk management frameworks and guidelines

Many countries follow risk management frameworks to regulate the safety of drinking and recreational water bodies (Chorus, 2012; Ibelings et al., 2014). In Argentina, there are no national regulations in force addressing a Risk Management Framework or dealing with the assessment of cyanobacterial or cyanotoxin presence. However, some water utilities have implemented either or both (Otaño et al., 2012).

As regards drinking water, most treatment plants have not incorporated routine analyses as of now, and only a few plant operators or safe water supervisory authorities apply monitoring programs following the Alert Levels or the provisional guideline for MC-LR of $1\ \mu g\ L^{-1}$ suggested by WHO (Chorus and Bartram, 1999; Otaño et al., 2012). To date, saxitoxins determination is carried out in treatment plants located in the north-eastern Argentina of the country (region 2, Otaño, personal communication), and anatoxin-a determination is performed only in region 3, where water from San Roque dam is analysed (Otaño et al., 2012). The "Control of Algal Bloom" program adopted by the Interjurisdictional Authority of the Limay, Neuquén and Negro River Basin (AIC, http://www.aic.gob.ar; region 5) is an example. Frequent blooms of *Dolichospermum* species in Ramos Mexía and Arroyito reservoirs led to water purification problems. The AIC developed specific contingency plans that included regular motoring/alert systems based on cyanobacterial biomass and communication to drinking water suppliers (Casco et al., 2014). Monitoring programs have also been put in place to survey water quality from Paraguay and Paraná rivers (Otaño, personal communication, http://www.aguasdecorrientes.com/).

Cyanobacterial dominance in Argentinean water bodies is most pronounced during the warmer months (summer-autumn), when the demand for recreational water is highest, as seen in other temperate regions (Chorus and Bartram, 1999; Funari et al., 2017). More efficient and affordable monitoring strategies are needed in recreational and bathing areas to develop frameworks of thresholds and actions to prevent cyanotoxin exposure for health surveillance and public communication systems. In this sense, the Administration Commission of the Uruguay River (Argentinean-Uruguayan Binational Commission, CARU), has been carrying out the Surveillance Program for the Uruguay River beaches since 2011. This monitoring program aims to assess the quality of recreational water located in Salto Grande reservoir and the

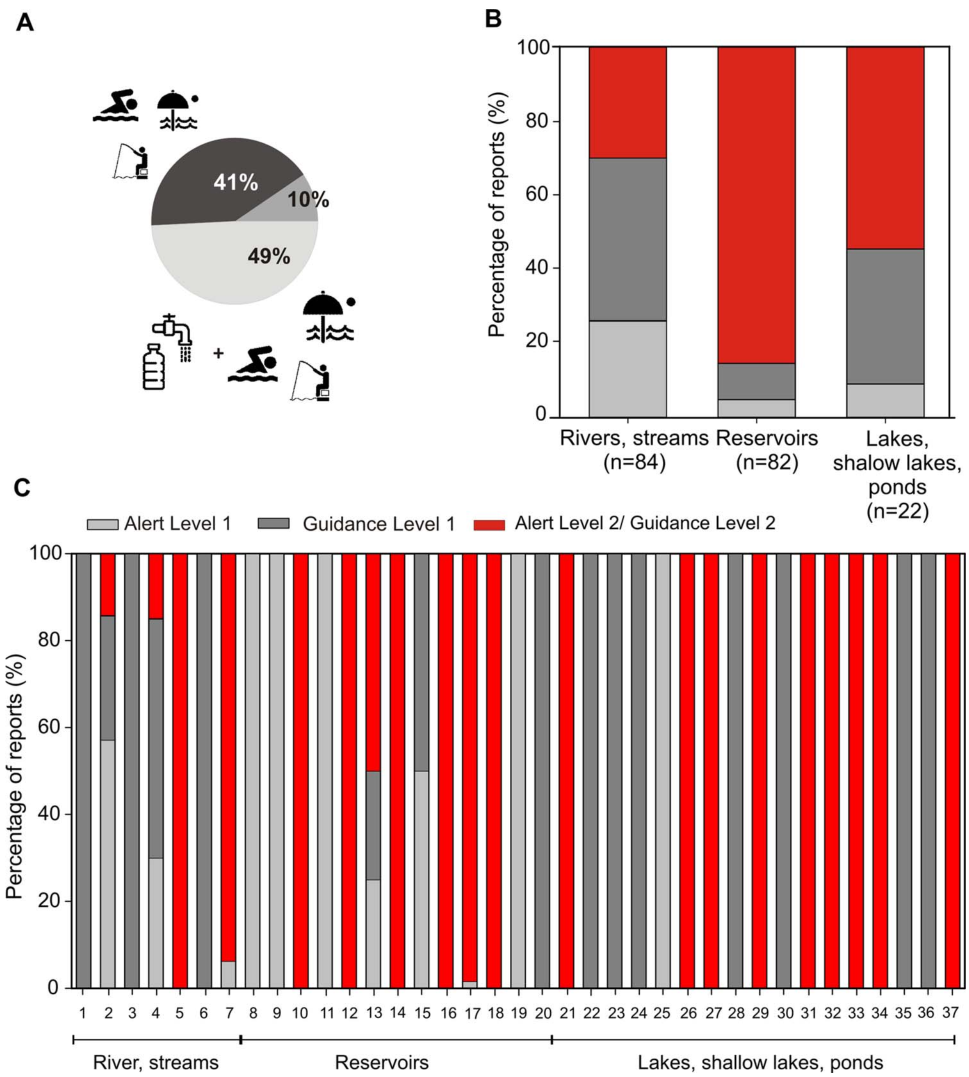

Fig. 5. Exposure routes and guidance values in Argentina. (A) Uses of affected water bodies ($n = 63$). Icons made by Freepik from www.flaticon.com. (B) Exposure risk associated with cyanobacterial biomass present in drinking waters and sources used for recreational purposes, according to Chorus and Bartram (1999). (C) Exposure risk associated with cyanobacterial biomass in freshwaters surveyed. For drinking waters, Level 1 (light grey bars) corresponds to cyanobacterial cell counts of 2000 cells mL^{-1} (or $0.2\ mm^3\ L^{-1}$ biovolume or $1\ \mu g\ L^{-1}$ chlorophyll *a* in the water body) and Alert Level 2 (red bars) corresponds to 100,000 cells mL^{-1} (or $10\ mm^3\ L^{-1}$ biovolume or $50\ \mu g\ L^{-1}$ chlorophyll *a*). For recreational waters, Guidance Level 1 (dark grey bars) corresponds to cyanobacterial cell counts of 20,000 cells.mL^{-1}(or $2\ mm^3\ L^{-1}$ biovolume or $10\ \mu g\ L^{-1}$ chlorophyll *a*) and Guidance Level 2 (red bars) corresponds to cyanobacterial cell counts of 100,000 cells mL^{-1} (or $10\ mm^3\ L^{-1}$ biovolume or $50\ \mu g\ L^{-1}$ chlorophyll *a*). Potential human health risk in recreational waters is considered low at Guidance Level 1, moderate at Guidance Level 2, and high when cyanobacterial cell concentration exceeds 100,000 cells.mL^{-1}(visible scum formation) (Chorus and Bartram, 1999; WHO, 2003). 1, Limay River ($n = 2$); 2, Paraná River ($n = 7$); 3, Reconquista River ($n = 1$); 4, Río de la Plata Estuary ($n = 60$); 5, Salado River ($n = 1$); 6, San Miguel stream ($n = 1$); 7, Uruguay River ($n = 16$); 8, Cabra Corral ($n = 1$); 9, El Tunal ($n = 1$); 10, Florentino Ameghino ($n = 1$);11, La Viña ($n = 1$); 12, Mari Menuco ($n = 3$); 13, Paso de las Piedras ($n = 4$); 14, Piedras Moras ($n = 1$); 15, Ramos mexía ($n = 2$); 16, Río Tercero ($n = 1$); 17, Salto Grande ($n = 62$); 18, San Roque ($n = 4$); 19, Urugua-í ($n = 1$); 20, Yaciretá ($n = 1$); 21, Artificial pond ($n = 1$); 22, Cava Los Talas ($n = 1$); 23, Chascomus ($n = 2$); 24, Cacique Chiquichano ($n = 1$); 25, Fagnano Lake ($n = 1$); 26, La Helvecia ($n = 1$); 27, Laguna Grande ($n = 2$); 28, Lobos ($n = 1$); 29, Los Patos ($n = 3$); 30, Pellegrini lake ($n = 1$); 31; Planetario lake ($n = 1$); 32, Salada Monasterio ($n = 1$); 33, San Jorge ($n = 2$); 34, Suco ($n = 1$); 35, Todos los Santos ($n = 1$); 36, Willimanco lagoon ($n = 1$); 37, Zeta Lagoon ($n = 1$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Uruguay River, and includes physicochemical and biological analysis. Reports on the presence or absence of cyanobacterial blooms in public beaches are posted in the CARU web page (http://www.caru.org.uy/) on a weekly basis during summers or monthly during the rest of the year.

In short, the frequency of cyanobacterial blooms in Argentina shows an urgent need for a federal Risk Management Framework concerning water quality criteria, management of harmful algal blooms and cyanotoxin surveillance.

5. Summary and conclusions

Toxic cyanobacterial blooms affect important water supplies and recreational areas located all over the country. The highest incidence is concentrated in central and eastern areas of Argentina (Río de la Plata Basin and Pampean region in the Chaco-Pampean Plain, reservoirs and dams in the arid region of the Peri-Pampean Sierras), which are the most densely populated regions in the country and are significantly impacted by agro-industrial activities.

Microcystis, Dolichospermum, *Raphidiopsis*, *Cylindrospermopsis* and *Planktothrix,* known cyanotoxins producers are the most prevalent bloom-forming genera associated with blooms. Their frequent occurrence in bloom concentrations suggests a high risk of exposure to toxigenic cyanobacteria and cyanotoxins through both drinking and recreational waters. In cases with quantitative cyanotoxin data, MC concentrations reach values that would compromise water consumption, and data showing whether treatment technologies are sufficiently effective in mitigating them are lacking. Cyanobacterial levels found in recreational areas often exceed the concentrations calling for warnings in the WHO scheme for cyanobacterial surveillance.

MCs are the most frequently encountered toxins, most likely because the cyanotoxin analyses available to date have focused on this group. However, the presence of blooms of potential saxitoxins or anatoxin-a and anatoxin-a(s) producers, together with recent records of such toxins, suggest that they may be both relevant and increasing, and thus highlight the need for monitoring.

Toxic cyanobacterial blooms are predicted to increase due to climate change and eutrophication. Guideline values and alert level frameworks at national and regional scales are therefore important in order to protect public health. This review shows the need to implement management policies and risk assessment in Argentina.

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